

How can we think outside the box and develop alternative atmospheric biosignatures?

NExSS workshop, July 2016

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Slides from the NExSS workshop, July 27th 2016.

Some of this material is unpublished, so I would be grateful if you could treat it appropriately. Published material is from the references listed on Slide31.

William Bains, July 2016.



Approach

- 1) based on understanding of why life does what it does
 - What is life?
 - Why does it make any gas/volatile?
 - What would it make in another (chemical) environment?
- 2) based on admitting we do not really know why life does what it does (mostly)
 - Exhaustive list
 - Start on rational identification of candidates



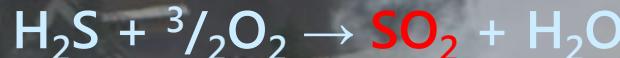
Biochemistry of gases

- Why do organisms make volatile compounds (=gases...)?



Biosignature gases

- Classified on why life makes them
 - Type I: byproduct of energy capture
 - Type II: byproduct of biomass capture
 - Type III: no chemical “reason” at all



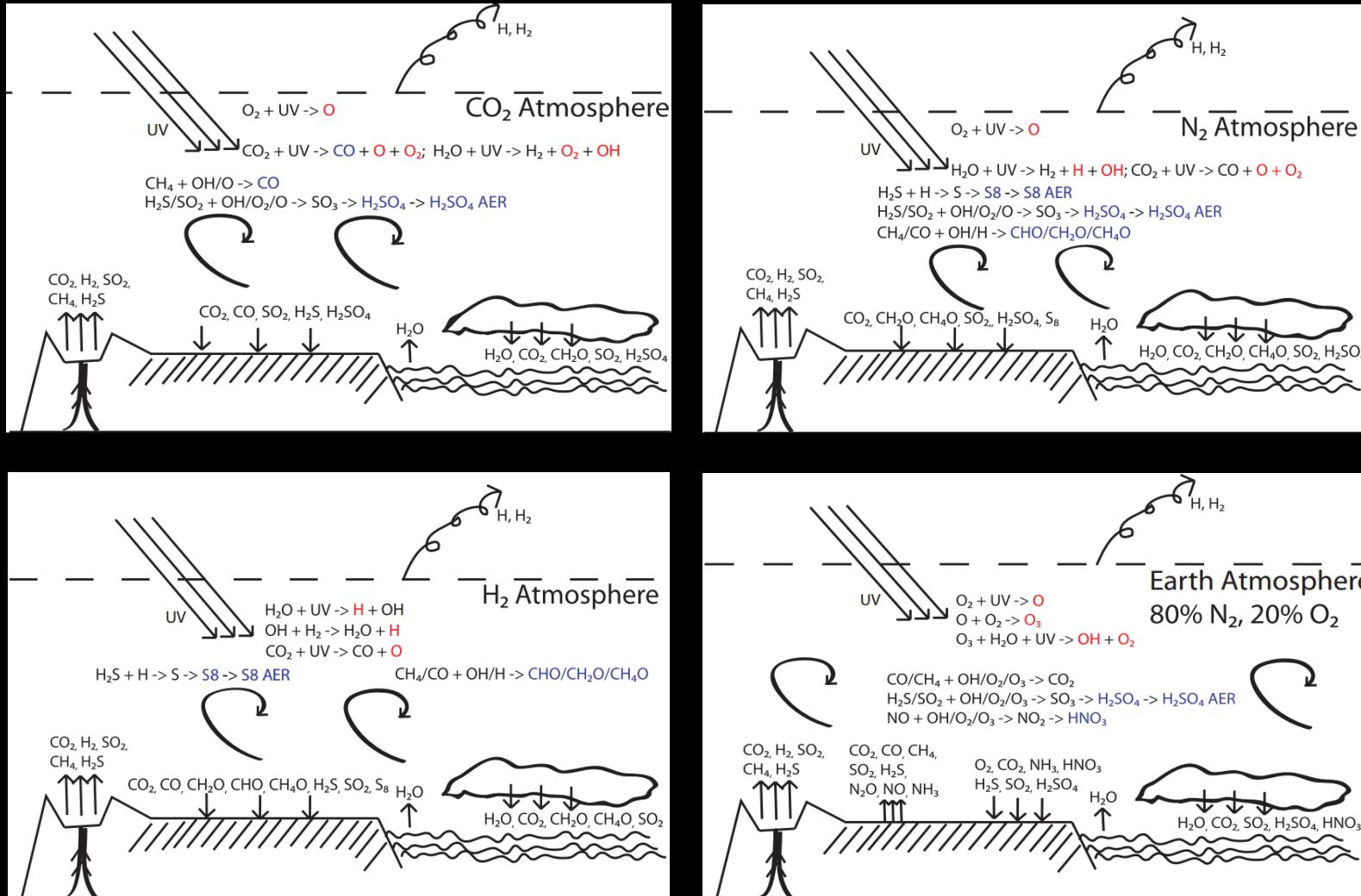
Type I

- Generated from exploitation of geochemical redox couples

Reductant	Oxidant	Products	Reductant	Oxidant	Products
H ₂	NO ₃ ⁻ →	NO ₂ ⁻ , H ₂ O	Organics	SO ₄ ²⁻ →	SO ₃ ²⁻ or SO ₂ , H ⁺
H ₂	NO ₂ ⁻ →	NO, H ₂ O	H ₂	SO ₄ ²⁻ →	SO ₃ ²⁻ or SO ₂ , H ⁺
H ₂	NO →	N ₂ O, H ₂ O	H ₂	SO ₃ ²⁻ →	S ₂ O ₃ ⁻ , H ⁺
H ₂	N ₂ O →	N ₂ , H ₂ O	H ₂	S ₂ O ₃ ⁻ →	S°, H ⁺
Fe ²⁺	NO ₃ ⁻ →	NO ₂ ⁻ , Fe ³⁺	H ₂	S° →	H ₂ S, H ⁺
Fe ²⁺	NO ₂ ⁻ →	NO, Fe ³⁺	CH ₄	SO ₄ ²⁻ →	H ₂ S, CO ₂
Fe ²⁺	NO →	N ₂ O, Fe ³⁺		<i>Oxidised</i>	
Fe ²⁺	N ₂ O →	N ₂ , Fe ³⁺		<i>Reduced</i>	
NH ₃ /NH ₄ ⁺	NO ₂ ⁻ →	N ₂ , H ₂ O		Carbon Dioxide (CO ₂)	Hydrogen (H ₂)
				Formic acid (HCO ₂ H)	Methane (CH ₄)
					Methanol (CH ₃ OH)
Input Molecules	Photon			Outputs	
H ₂ O	hν	→	O ₂	Ethanol (C ₂ H ₅ OH)	
H ₂ S	hν	→	S	Lactate (CH ₃ .CHOH.CO ₂ H)	
S ₂ O ₃ ⁻	hν	→	H ₂ SO ₄	Acetone (CH ₃ .CO.CH ₃)	
S, H ₂ O	hν	→	H ₂ SO ₄	Butyric acid (C ₃ H ₇ CO ₂ H)	



Type I prediction



Type I products on H₂-dominated worlds

Element	Reaction	ΔG° (kJ/mol)
Carbon	CO + 3 H ₂ → CH ₄ + H ₂ O	-205.6
	CO ₂ + 4H ₂ → CH ₄ + 2H ₂ O	-194.5
	CO ₂ + H ₂ → CO + H ₂ O	+11.5
	CO ₃ ²⁻ + 4H ₂ → CH ₄ + H ₂ O + 2OH ⁻	-129.42
Nitrogen	½ N ₂ + ½ H ₂ → NH ₃	-62.61
	½ N ₂ + ½ H ₂ + H ₂ O → NH ₂ OH	+183.8
Phosphorus	H ₂ + HPO ₄ ²⁻ → HPO ₃ ²⁻ + H ₂ O	+27.2
	H ₂ + HPO ₃ ²⁻ + H ⁺ → H ₂ PO ₂ ⁻ + H ₂ O	+84.3
	½H ₂ + H ₂ PO ₂ ⁻ + H ⁺ → P _(s) + 2H ₂ O	+52.8
	P _(s) + ½H ₂ → PH ₃	+5.4
	Overall 4 H ₂ + HPO ₄ ²⁻ + 2H ⁺ → PH ₃ + 4H ₂ O	+169.8
Sulfur	SO ₄ ²⁻ + H ₂ → SO ₃ ²⁻ + H ₂ O	+12.45
	SO ₃ ²⁻ + 2H ₂ + 2H ⁺ → S _(s) + 3H ₂ O	-248.29
	S _(s) + H ₂ → H ₂ S	-44.81
	Overall SO ₄ ²⁻ + 2H ⁺ + 4H ₂ → H ₂ S + 4H ₂ O	-280.8
Iron	½ H ₂ + Fe ³⁺ + OH ⁻ → Fe ²⁺ + H ₂ O	-125.8
	H ₂ + Fe ²⁺ + 2OH ⁻ → Fe _(s) + 2H ₂ O	-6.1
Manganese	Mn ³⁺ + ½ H ₂ + OH ⁻ > Mn ²⁺ + H ₂ O	-273.3
	H ₂ + Mn ²⁺ + 2OH ⁻ → Mn _(s) + 2H ₂ O	-24.9
Silicon	2H ₂ + H ₄ SiO ₄ _(s) → Si _(s) + 4H ₂ O	+384.5
	2H _{2(g)} + SiO _{2(s)} > Si _(s) + 2H ₂ O	+382.1
	Si _(s) + 2H _{2(g)} → SiH _{4(g)}	+56.9
Aluminium	3H _{2(g)} + Al ₂ O _{3(s)} → 2Al _(s) + 3 H ₂ O	+871.0
Copper	Cu ²⁺ + ½H ₂ → Cu ⁺ + H ⁺	-19.4
	Cu ⁺ + ½ H ₂ → Cu _(s) + H ⁺	-57.8
Vanadium	H ₂ VO ₄ ⁻ + 2H ⁺ + ½H ₂ → HVO ₂ ⁺ + 2H ₂ O	-113.8
	HVO ₂ ⁺ + ½H ₂ → VO ⁺ + H ₂ O	-243.5
	VO ⁺ + ½ H ₂ → VOH ⁺	17.5
	VOH ⁺ + H ₂ → V _(s) + H ⁺ + H ₂ O	122.7

- Plausible substrates

- Volatile products

- 25°C temp

-CH₄, H₂S, H₂O, NH₃



Type I

- Atmospheric chemistry
- Biosignature gas constantly removed
- Flux needed to maintain a detectable gas level
- Reaction chemistry and Maintenance Energy
- Biomass needed to maintain a detectable gas level
- *Is that reasonable??*



Live biomass densities



	Sun-like star	Active M star	Quiet M star
Thermal emission	4.0×10^{-4} (g/m²)	8.0×10^{-6} (g/m²)	9.5×10^{-6} (g/m²)
Transmission	-	1.1 (g/m²)	1.8×10^{-9} (g/m²)



10 - 50g/m²



50 – 1000 g/m²

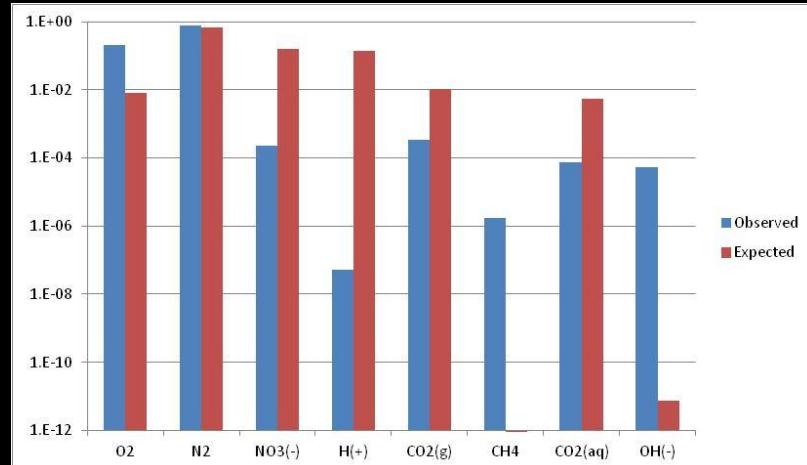


0.01g/m²

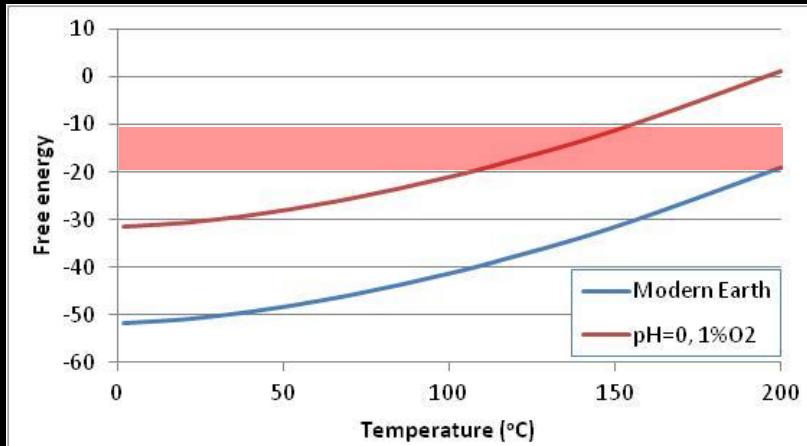


Problems

- False positives
 - Geochemistry has same chemicals to work with
 - E.G. methane on Mars?
- False negatives
 - $\text{N}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$
 - abundant source gas
 - BEQ

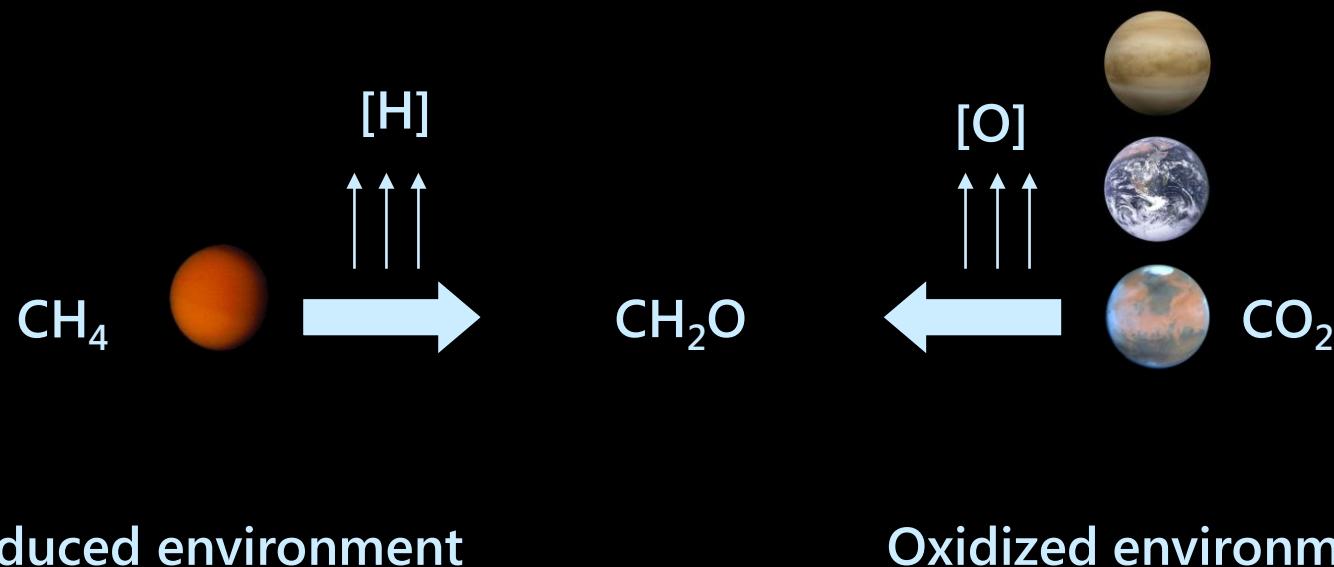


From Krissansen-Totton et al 2016 Table 7



Redox signature *necessary*

- 'Problem' for life
- To access large chemical space, need molecules R_r 0.5 – 0.9
- Environmental carbon in *dense* bodies



Redox signature in presence of H₂

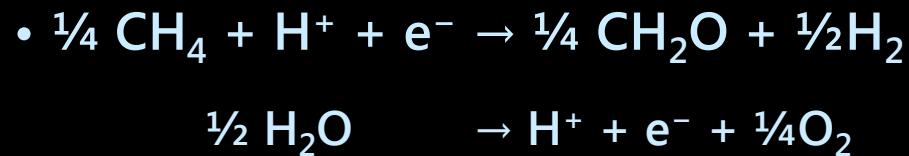
Outgassing	Other process	Atmospheric carbon
CO ₂ / CO	-	H ₂ + 10:1 CO ₂ :CH ₄
CO ₂ / CH ₄	-	H ₂ + 50:50 CO ₂ :CH ₄
CO ₂ / CH ₄	CO ₂ + H ₂ → CH ₄	H ₂ + 1:99 CO ₂ :CH ₄

- Type II signature
- CH₄ + H₂O + energy → [CH₂O]_n + [H]
- Most plausibly
- CH₄ + H₂O + energy → [CH₂O]_n + H₂

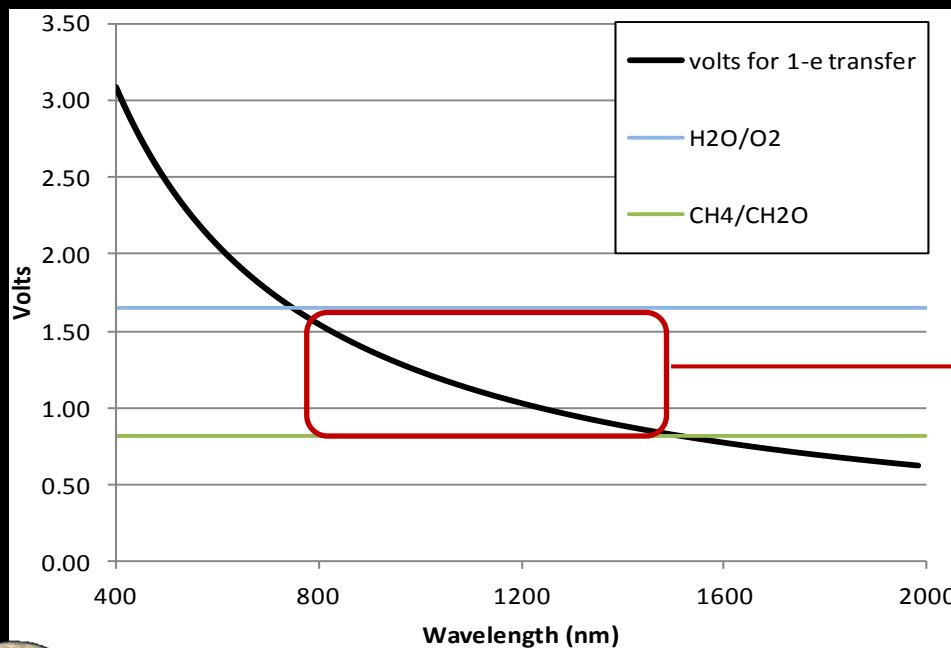
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Photon energy



$$\left. \begin{aligned} E^\circ &= 0.63 \text{ V} \\ E^\circ &= 1.23 \text{ V} \end{aligned} \right\} + \text{overvoltage}$$



Absorption in NIR
→ no 'Red Edge'?



14



Type III

- Range terrestrial Type III gases.
- Assume maximum terrestrial emission rates / gram biomass

Biomass needed to maintain detectable levels of Type III gases in atmosphere of 1bar H ₂ -dominated atmosphere planet in 'habitable zone' around different stars (g/m ²)					
Compound	Thermal emission			Transmission	
	Sun-like	Active M-star	Quiet M-star	Active M-star	Quiet M-star
CH ₃ Cl	2800	77	0.013	860	0.014
DMS	190	82	0.0001	260	0.00036
CS ₂	5.5×10^7	2.3×10^7	37	1.5×10^7	24
OCS	1.3×10^5	5500	0.67	9.9×10^4	12



Type III

- Range of studies on terrestrial Type III gases.
- Assume maximum terrestrial emission rates / gram biomass

Biomass needed to maintain detectable levels of Type III gases in atmosphere of 1bar H ₂ -dominated atmosphere planet in 'habitable zone' around different stars (g/m ²)					
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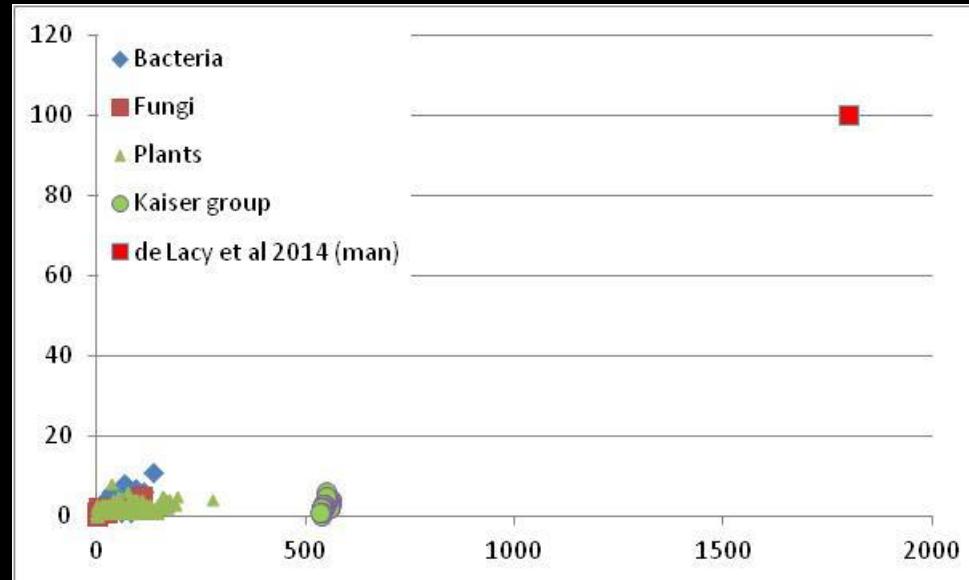
CF ...



But ...

- What is collected?

- What is known?



GEN News Highlights

Jul 27, 2016

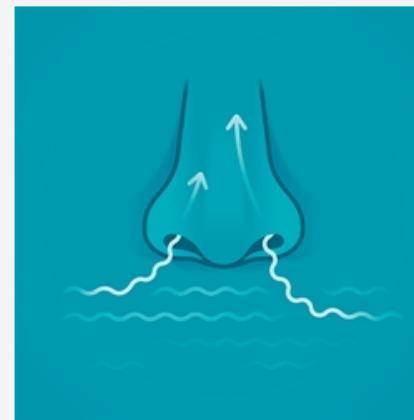
Sniffing Out Alzheimer's

What if it were possible to predict cognitive decline and detect the early stages of Alzheimer's disease (AD) based on the results of an odor identification test? A group of New York neuroscientists believe this is possible on the basis of their recent discoveries. Researchers from Columbia University Medical Center (CUMC), New York State Psychiatric Institute, and NewYork-Presbyterian presented data at the Alzheimer's Association's International Conference in Toronto from two studies that suggest the University of Pennsylvania Smell Identification Test (UPSIT) may offer a practical, low-cost alternative to other current diagnostic tools for predicting AD.

In one study—"Predictive Utility of Entorhinal

[More »](#)

Click Image To Enlarge +



Researchers have reported that an odor identification test may prove useful in predicting cognitive decline and detecting early-stage Alzheimer's disease.
[f1o/Getty Images]

Market & Tech

- Race to Find Better miRNA Detection
- Epigenetics Marks Qualitative and Quantitative Picture
- Growing Outsourcing Discovery Activities
- A 10,000-Foot View of the Cell Market Landscape
- For Struggling Pharms, Vaccines Offer Path to Recovery

Be sure to take a look at our

Scientifically Studied

MDMA (commonly known as "ecstasy") is classified as a Schedule I drug, which is reserved for compounds with no accepted medical use and a high potential for abuse. However, researchers have, however, call for a rigorous examination of MDMA's effects to identify its therapeutic potential. Two researchers, however, call for a rigorous examination of MDMA's effects to identify its therapeutic potential. Two researchers, however, call for a rigorous examination of MDMA's effects to identify its therapeutic potential. Two researchers, however, call for a rigorous examination of MDMA's effects to identify its therapeutic potential.



EG halomethanes

Made by life	Not known to be made by life
CH_4 	

- There are 34 possible halomethanes (excluding F). 22 are produced by Earth's life. 12 are not known to be produced. Why?
- Why not CFCs?
- Terrestrial life rarely handles F
- 2.4Gya rarely handled O



All Small Molecules project

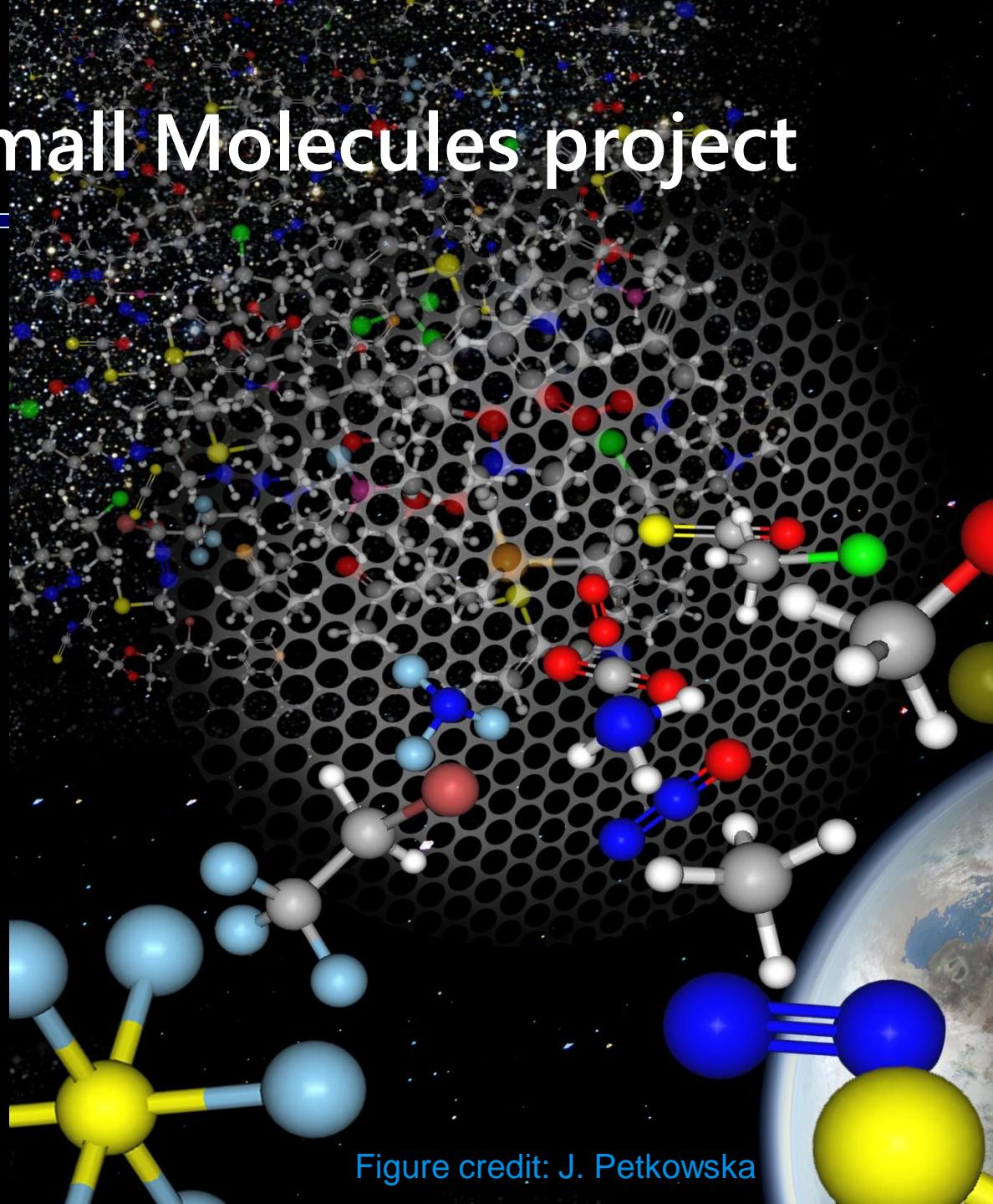
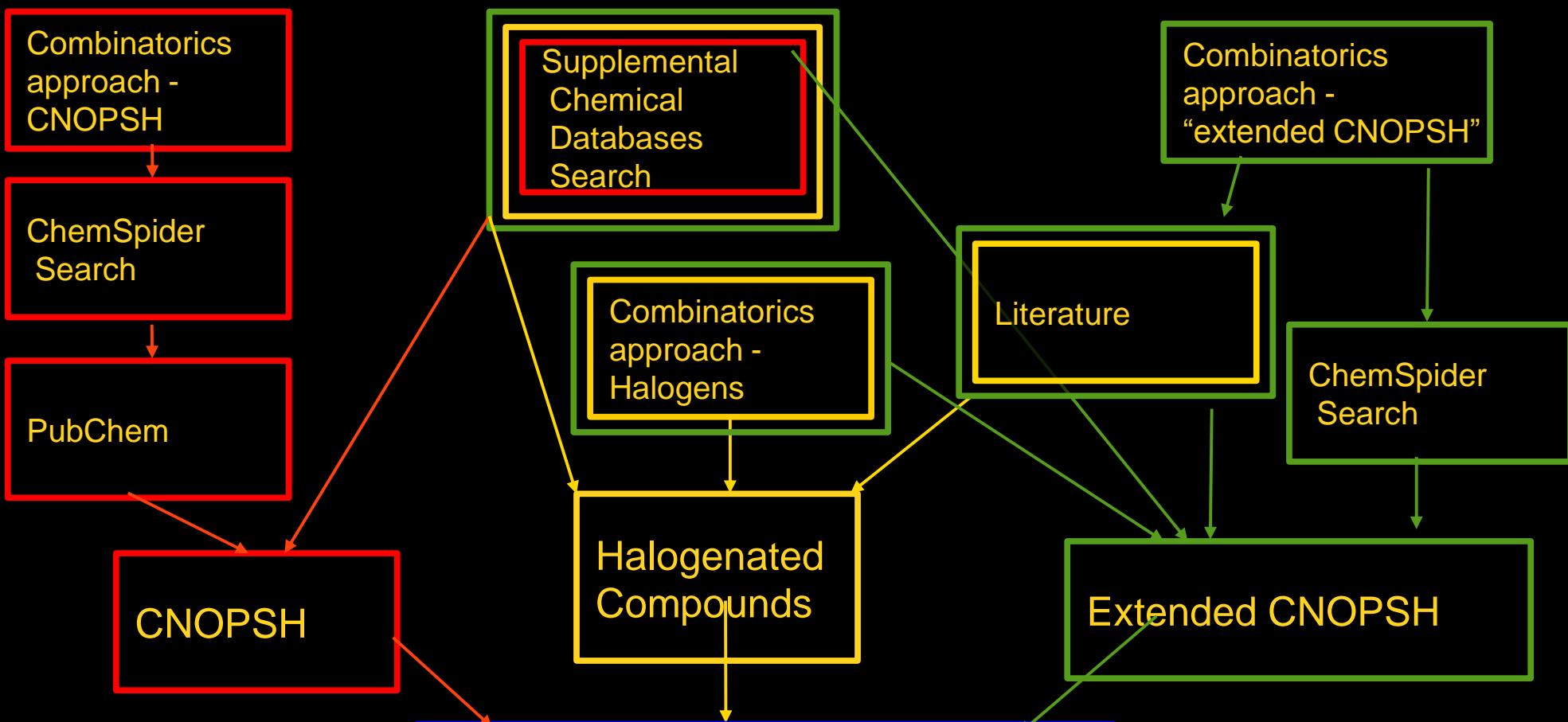


Figure credit: J. Petkowska



PBS database construction



Petkowski, Bains, Seager

**COLLECTION OF ~14k STABLE
VOLATILE CHEMICALS up to
 $N < 7$ non-H atoms**

Seager et al 2016



IUPAC name	Molecular Formula	Molecular Weight (Da)	SMILES	Boiling point (°C)	Produced by life Y/N	Reference for production by life
N,N-Dimethylmethanamine	C3H9N	59.11	CN(C)C	4(e)	Y	Kite, G.C. and Hetterscheid, W.L.A. 1997
Buta-2,3-dien-1-amine	C4H7N	69.1	NCC=C=C	88(p)	N	
3-Buten-2-amine	C4H9N	71.12	C=CC(C)N	73(p)	N	
2-Oxiranecarbaldehyde	C3H4O2	72.06	O=CC1OC1	96(p)	N	
N-Ethylethanamine	C4H11N	73.14	CCNCC	55(e)	Y	Smith, B.N. and Meeuse, B.J.D. 1966
Hydrazinecarboxamide	CH5N3O	75.07	NNC(N)=O	210(p)	Y	van Poucke, C. et al. 2011
Amino(hydroxyamino)methanol	CH6N2O2	78.07	OC(N)NO	221(p)	N	
Cyclopropylmethanethiol	C4H8S	88.17	SCC1CC1	111(p)	N	
1,3-Dithietane 1-oxide	C2H4OS2	108.18	O=S1CSC1	198(p)	N	
Methyl hydrogen carbonotriethioate	C2H4S3	124.25	S=C(S)SC	200(p)	N	
(...)						
Stibine	H3Sb	124.78	[SbH3]	-18(e)	Y	Michalke, K. et al. 2000
3-(Methylselanyl)-1-propene	C4H8Se	135.07	C[Se]CC=C	113(p)	N	
Tetrahydroselenophene	C4H8Se	135.07	[Se]1CCCC1	128(p)	N	
2-(Methylselanyl)-1-propene	C4H8Se	135.07	[Se](C(=C)C)C	107(p)	N	
N,N-Dimethylselenoformamide	C3H7NSe	136.05	[Se]=CN(C)C	120(p)	N	
Se-Methyl ethaneselenoate	C3H6OSe	137.04	O=C([Se]C)C	137(p)	N	
Methylstibine	CH5Sb	138.81	C[SbH2]	41(e)	Y	Wehmeier, S. et al. 2005
[(Methylselanyl)sulfanyl]methane	C2H6SSe	141.09	C[Se]SC	135(p)	N	
3-(Methyltellanyl)-1-propene	C4H8Te	183.71	[Te](CC=C)C	111(p)	N	
Monomethyl bismuth hydride	CH5Bi	226.03	C[BiH2]	80(p)	Y	Meyer, J. et al. 2008
(...)						
Bromotrichloromethane	CBrCl3	198.27	C(Cl)(Cl)(Cl)Br	105(e)	N	
Bromodiiodomethane	CHBrI2	346.73	IC(I)Br	221.5(p)	Y	Gribble, G. 2003
Chlorotribromomethane	CBr3Cl	287.18	C(Cl)(Br)(Br)Br	86(p)	N	
Trichloroacetonitrile	C2Cl3N	144.38	N#CC(Cl)(Cl)C	84(e)	Y	Ballschmiter, K. 2003
1-Fluoropropane	C3H7F	62.09	CCCF	114(p)	N	
Tetrafluoromethane	CF4	88	C(F)(F)(F)F	-150(e)	N	
Cyanic chloride	CNCI	61.47	C(#N)CI	123(p)	N	
2-Bromo-1,1-dichloroethene	C2HBrCl2	175.84	C(=C(Cl)Cl)Br	109(p)	Y	Nightingale, P.D. et al. 1995
Sulfur hexafluoride	SF6	146.06	FS(F)(F)(F)(F)F	-64(e)	N	
Trichloroamine	NCI3	120.37	N(Cl)(Cl)Cl	71(e)	N	
(...)						

Stuff that (non-industrial)
terrestrial life is *extremely unlikely*
to make

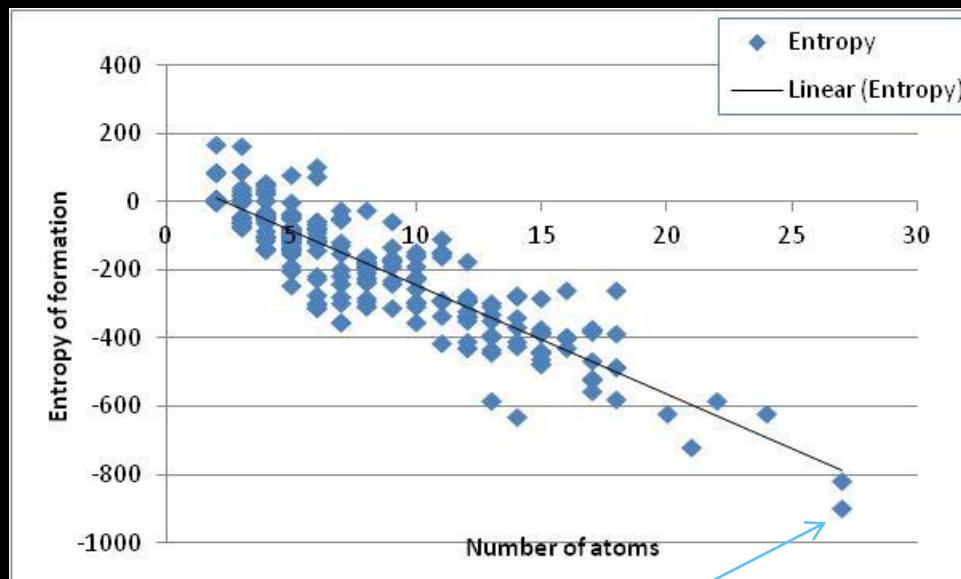


What next

- NIR detectability
- Known geochemical production
- Thermodynamics
 - Given range of modelled surface geochemistry
 - Local? Globally averaged?
 - E.g . Entropy of formation as guide

$$\Delta G = \Delta H - T \cdot \Delta S$$

- Develop 'geochemistry plausibility index'



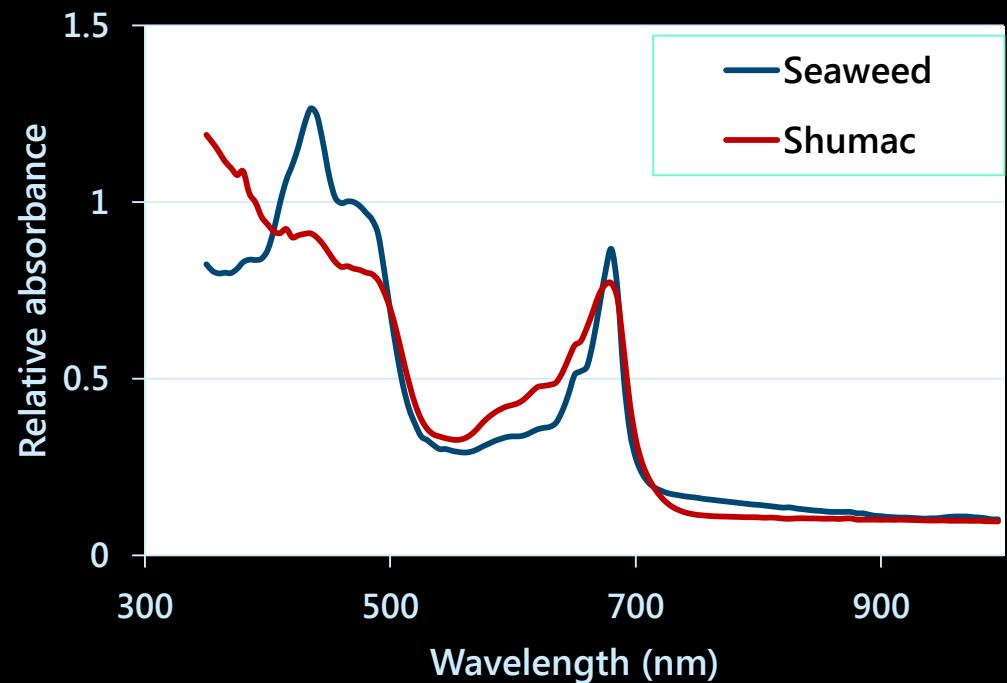
280 small volatile molecules, CHONSP + B, Si, As, Ge

Dimethylwotzahoozy
(thanks, Vikki...)



What about surface / pigment signatures?

- What colour is life on Earth?
- Why?
- 'Red Edge' ...
- Hence – what pigments?



Colour of life

- Can you derive colour from function?
- Light harvesting
- UV/light protection
 - Melanin
- Visual signalling
 - Anything!
- Accidental colour
 - E.g. polyphenols



Oh, Ok, let's do the Red Edge



850-1000nm



What alien cows would look like



Colour of life

- Can you derive colour from function?
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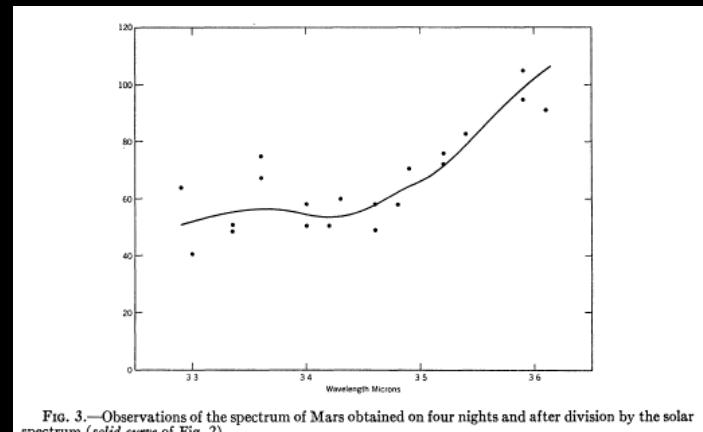
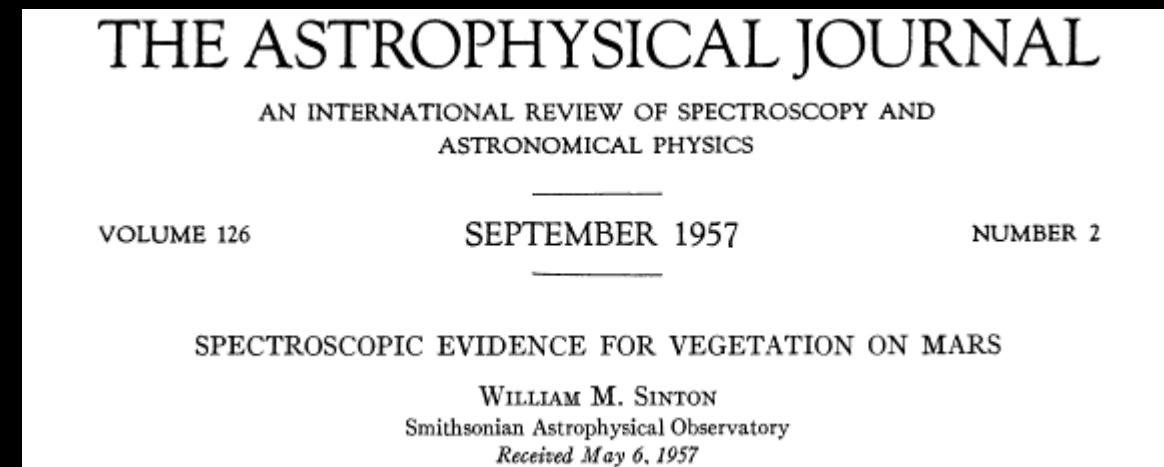
<http://biosignatures.astro.cornell.edu/>



Colour of life

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Easily mimicked?



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No man is an island ...



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How can we think outside the box and develop alternative atmospheric biosignatures?

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